EUROPEAN COMMISSION
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Institute for Reference Materials and Measurements

Certification of the specific micropore volume and the median micropore width of two microporous reference materials according to Draft-DIN 66135-4

BCR-704
BCR-705

B. Röhl-Kuhn, P. Klobes, K. Meyer, P. Lorenz, B.M. Gawlik, A. Lamberty, H. Muntau

Report EUR 21065

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European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

Tel.: +32 (0)14 571211
Fax: +32 (0)14 590406

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

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REFERENCE MATERIALS

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B. Röhl-Kuhn, P. Klobes, K. Meyer, P. Lorenz

Federal Institute for Materials Research and Testing (BAM)
D-12200 BERLIN (Germany

B.M. Gawlik, A. Lamberty

European Commission, DG Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
B-2440 GEEL (Belgium)

H. Muntau

Università degli Studi di Sassari, Sede Gemmata di Nuoro
I-08100 NUORO (Italy)

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ABSTRACT

This report describes the certification of the specific micropore volume and the median micropore width of two microporous reference materials (zeolites with 1-2 % clay as binder) according to Draft-DIN 66135-4 [1]. The adsorptive used for both materials was argon at the temperature of liquid argon. The report contains all the results of the 10 participating laboratories using 12 instruments. Furthermore, the data concerning the homogeneity and the stability studies are summarised. The Langmuir specific surface area and the density measured by helium gas pycnometry are given as indicative values.

Certified values were accompanied by an expanded uncertainty according to the requirements laid down in the Guide for the Expression of Uncertainty in Measurement (GUM) [2].

BCR-704 (adsorption of argon at 87 K)[1]

Certified property	Certified value[2]	Uncertainty[3]	Unit	No. of data sets
Micropore volume	0.205	0.006	$cm^3\ g^{-1}$	12
Median micropore width	0.668	0.019	nm	12

BCR-705 (adsorption of argon at 87 K)[1]

Certified property	Certified value[2]	Uncertainty[3]	Unit	No. of data sets
Micropore volume	0.181	0.006	$cm^3\ g^{-1}$	12
Median micropore width	0.592	0.020	nm	12

(1) The results are specific to Draft DIN 66135-4

(2) This values are the unweighted mean of accepted means obtained independently by seven different laboratories

(3) Expanded uncertainty with a coverage factor of k=2 according to the GUM [2].

LIST OF ABBREVIATIONS AND SYMBOLS

$A_{Langmuir}$	Langmuir surface area
$a_{Langmuir}$	slope of the regression line of the Langmuir plot
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BAM	Bundesanstalt für Materialforschung und -prüfung
BCR	Community Bureau of Reference
BET	Brunauer, Emmett, Teller
CRM	Certified reference material
$\Delta m/m_t$	mass loss in % of sample mass
DIN	Deutsches Institut für Normung
ISO	International Standard Organization
IUPAC	International Union of Pure and Applied Chemistry
LGC	Laboratory of the Government Chemist
n	number of replicate measurements
n_{Lab}	number of laboratory means
N_A	Avogadro constant
NIST	National Institute of Standards and Technology
p	Pressure of the adsorptive in equilibrium with the adsorbent
p_0	Saturation vapour pressure of the adsorptive
p/p_0	Relative pressure
p_{st}	Standard pressure (= 1.01325 10^5 Pa = 760 Torr)
s	Standard deviation of laboratory means
STP	Index denoting the standard state ("at standard temperature T_{st} and pressure p_{st}")
$s/\sqrt{n}$	Standard uncertainty of the certified value
σ_{Ar}	Molecular cross-sectional area for argon (= 0.142 nm^2)
u_{bb}	uncertainty contribution for the inhomogeneity included in U_{CRM}
u_{char}	uncertainty contribution for the batch characterisation included in U_{CRM}
u_{sts}	uncertainty contribution for the short-term stability of the material (transportation, not included in U_{CRM})
u_{lts}	uncertainty contribution for the long-term stability of the material (storage) included in U_{CRM}
U_{CRM}	expanded uncertainty of the certified value
T	Temperature
V_a	Adsorbed gas volume
V_m	Monolayer capacity (at STP)
V_{mol}	Molar gas volume (at STP) (= 0.022414 $m^3\ mol^{-1}$)

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1. INTRODUCTION

Porous and highly dispersed materials represent a specific state of solids and have numerous applications in research and industry. Examples of applications are catalysts, pigments, building materials, and pharmaceutical products. Porous materials are of great importance for the development and optimisation of such processes like sintering, chromatographic separation, and catalysed chemical reactions [3]. The development and provision of porous certified reference materials (CRMs) according to the BCR guidelines make an important contribution to the comparability of experimental outcomes. CRMs are necessary for the calibration of measurement instruments and the trueness of analytical results. In contrast to the certification of the element contents of RMs in which the procedure involves mostly different independent methods to determine the true value, the certification of the values of the specific surface area, pore size, and specific pore volume is method dependent. The porous CRMs to be developed in the project described here are intended for the method of gas adsorption which is based on the evaluation of measured adsorption isotherms (primary data) [4] as depicted in Fig. 1.

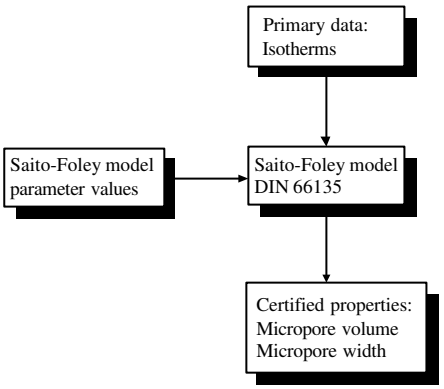

Figure 1 - Adherence to standardised procedures for assuring traceability

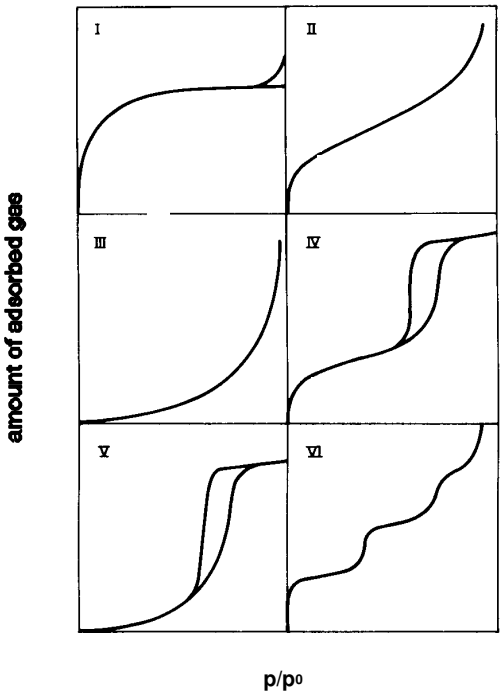

Figure 2 - Classification of isotherm types according to the IUPAC

Argon at its boiling point (87 K) is the adsorptive mostly used in connection with the micropore size analysis by means of the gas adsorption method. The method of gas adsorption takes advantage of the fact that the interactions between inert gases and surfaces of solids are weak (physisorption). However, even with the most elaborate *ab-initio* methods of quantum chemistry available today it is impossible to predict the adsorption behaviour of gases on real solids. For the evaluation of the measured isotherms, it is necessary to chose among the variety of evaluation procedures that procedure which is based on a theoretical model giving the best description of the isotherm. Figure 2 shows the classification of the isotherms according to the IUPAC [5]. The following types may be distinguished:

- Type I: These isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.
- Type II: In general, this type is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. The Type II isotherm represents unrestricted monolayer-multilayer adsorption.
- Type III: Isotherms of this type are convex to the p/p_0 axis over its entire range. They are not common, but there are a number of systems (e.g. nitrogen on polyethylene) which give isotherms with gradual curvature. In such cases, the adsorbate-adsorbate interactions play an important role.
- Type IV: Characteristic features of these isotherms are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high p/p_0. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are given by many mesoporous industrial adsorbents.
- Type V: Such isotherms are uncommon; they are related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak.
- Type VI: This type, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers. Amongst the best examples of Type VI isotherms are those obtained with argon or krypton on graphitised carbon blacks at liquid nitrogen temperature.

Subdivisions of the types I, II, III, and IV have been developed by Roquerol *et al.* [6].

When developing certified reference materials for the pore analysis by the gas adsorption, two important restrictive conditions must be taken into account. First, a general theory of physisorption for the entire p/p_0 range does not exist. Furthermore, standardised evaluation methods are available only for the isotherm types I, II, and IV of the IUPAC classification. Disperse and porous solids show fractal behaviour with respect to important pore properties [7].

It follows from a) that the material to be certified must strictly be selected according to a isotherm type of the IUPAC classification.

From b) one concludes for example that the experimentally determined value of the specific surface area for porous or highly dispersed solids depends on the size of the probe molecule [8]. Therefore, a true or absolute value of the specific surface area does not exist for fundamental reasons. Hence, the traceability for certified porosity properties can only be

assured by strictly applying standardised measurement procedures and evaluation methods (see Fig. 1). Another possibility consists in certifying the whole pressure/volume curve (isotherm).

The development of certified reference materials for the gas adsorption method at the European level started with the BCR products BCR-169 to -175 in 1989. The BCR report EUR 12025 [9] describes the certification of these six low specific surface area particulate reference materials. They consist of three aluminas with specific surface areas of 0.104, 1.05 and 2.95 m^2/g, a natural quartz (2.56 m^2/g), a rutile titania (8.23 m^2/g) and tungsten (0.181 m^2/g). Results for the surface area of a bronze (0.063 m^2/g), which was not certified, are also included. The specific surface area was calculated by means of the BET method [10-12]. Another CRMs for the BET specific surface area have also been produced by LGC and NIST [13]. LGC offers graphitised black carbon of 10.5 and 69, non-porous silica of 142, and mesoporous silica of 247 m^2/g, and NIST silica-alumina of 258.32, and two silicon nitrides of 10.52 and 2.85 m^2/g. BAM developed from 1993 to 1996 four porous CRMs using the gas adsorption method with the adsorptives nitrogen and krypton at the temperature of liquid nitrogen. A special certification procedure for meso- and microporous materials with isotherm types I, II, and IV according to the IUPAC classification was developed. Two of these CRMs were certified for specific surface areas as well as for their specific pore volume and pore width. These materials had been the first porous CRMs with certified quantities of pore volume and pore width on the basis of international standards and recommendations [4].

2. PARTICIPATING LABORATORIES

A total number of 10 laboratories from 6 European countries using 12 instruments (7 different types of instruments produced by 4 different companies, see Table A-15 in the Annex) took part in the interlaboratory comparison. The Bundesanstalt für Materialforschung und -prüfung (BAM) participated with 3 instruments (counted as 3 laboratories for the statistical data evaluation).

Co-ordination

Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin	DE

Preparation of the materials

Merck KGaA, Darmstadt	DE

Analyses

BP Chemicals Limited, Middlesex	UK
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin	DE
Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S, Marseille	FR
Delft University of Technology, Delft	NL
Friedrich-Schiller-Universität Jena, Jena	DE
Micromeritics Belgium, Diegem	BE
Quantachrome GmbH, Odelzhausen	DE
Universidad de Alicante, Alicante	ES
Universität Erlangen-Nürnberg, Erlangen	DE
Universiteit van Amsterdam, Amsterdam	NL

3. SELECTION AND CHARACTERISATION OF THE CANDIDATE MATERIALS

3.1 The nature of the starting materials

The following substances manufactured by the company Merck KGaA were selected as candidate materials:

1. for BCR-704: Faujasite type zeolite (FAU), a calcium aluminium silicate
2. for BCR-705: CaA-zeolite / Linde type A (LTA), a calcium exchanged sodium aluminium silicate

These microporous materials are pelletised substances with a diameter of about 2 mm (binder content: 1 - 2 % clay). The pellets were not crushed.

The substances were homogenised by means of a tumbling drum mixer. The procedures for the production including a special stabilisation of the materials and the homogenisation are documented at Merck KGaA.

3.2 Physical and chemical characterisation of the materials

3.2.1 Density

The "*apparent*" density was determined by helium pycnometry at room-temperature (296 K = 23 °C) after a drying at 393 K (= 120 °C) for 24 hours:

- BCR-704: 2.34 g/cm^3
- BCR-705 :2.36 g/cm^3

The term "*apparent*" density means the density of the material including closed and therefore inaccessible pores. The gas used was dry helium with a purity not less than 99.99 %.

3.2.2 Si/Al ratio of the zeolites BCR-704 and BCR-705

The zeolites BCR-704 and BCR-705 were characterised by the Si/Al ratio. As a result of ^{29}Si MAS NMR investigations, for the material BCR-705 a ratio of Si/Al = 1.0 was determined. This is in accordance with the cell content of $\{Na_{12}[Al_{12}Si_{12}O_{48}] \cdot 27\ H_2O\}_8$ for Linde type A (LTA) zeolites [14]. The Si/Al ratio for the material BCR-704, a faujasite type zeolite (FAU), was found to be Si/Al = 1.6 indicating a FAU specification type Y. The channels in these two zeolite materials (crystallographic free diameters determined by X-ray diffraction) are for BCR-704 (FAU) about 0.74 nm and for BCR-705 (Ca-exchanged LTA) about 0.5 nm [14].

3.2.3 Thermogravimetric investigations

Thermogravimetric investigations of the candidate materials are necessary to develop an optimum outgassing procedure for the products. Figure 3 contains the thermogravimetric curves of the two zeolites BCR-704 and BCR-705.

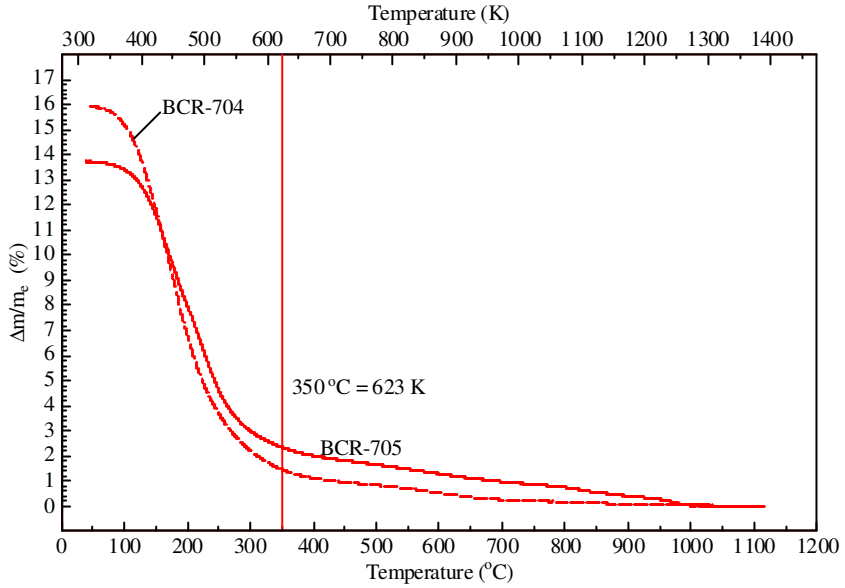

Figure 3 - Thermogravimetric curves of BCR-704 and BCR-705

3.3 Porosity characterisation

3.3.1 Methods used for the certification measurements

The values for the porosity properties to be certified were determined by means of the gas adsorption method. All instruments used in the interlaboratory comparison measured the amount of gas adsorbed at a certain relative pressure by the volumetric principle (gas adsorption manometry). The cumulative plot of the gas amount adsorbed at each dose step (ordinate) versus the relative pressure (abscissa) gives the adsorption isotherm (see Fig. 2). The isotherm data points represent the primary data of the gas adsorption method. All further quantities such as the specific surface area, the pore size distribution or the median pore width are calculated from the isotherm by means of special evaluation models.

Micropore volume and median micropore width were selected for the certification of microporous materials' porosity properties.

The specific surface area of both materials has not been certified because there are no standardised methods for the determination of the internal area of microporous materials. The BET model [10] is definitely not valid for microporous solids especially for pore widths < 0.7 nm and $p/p_0 < 0.01$ (primary pore filling region). At first glance, the classical Langmuir model should be more appropriate for determining the specific surface area of a microporous material but there is strong evidence that this model is an oversimplification which does not consider the real mechanism of micropore filling [6]. It is now generally agreed that the values of the total surface area of microporous solids as derived either by the BET or the Langmuir analysis are incorrect. Therefore, the results for the Langmuir specific surface area of both materials obtained here can only be regarded as informative values.

Micropore filling takes place at lower p/p_0 values than the capillary condensation in mesoporous solids. Investigations have shown that it is a quite different mechanism than capillary condensation [6].

One possible starting point for the theoretical treatment of the micropore size distribution is the Polanyi theory of the adsorption potential. By means of this theory, Horvath and Kawazoe [15] developed a model for slit shaped micropores. Saito and Foley [16] expanded the Horvath/Kawazoe model to cylindrical micropores.

The Langmuir specific surface area [17] is calculated by the relation:

$$A_{Langmuir} = \sigma_{Ar} \cdot N_A \cdot V_m / V_{mol} \qquad (1)$$

The monolayer capacity V_m (in $cm^3\ g^{-1}$ STP) is obtainable from the slope $a_{Langmuir}$ of the linear regression plot of the transformed isotherm points (the so called Langmuir plot) in which the values $(p/p_0)/V_a$ are plotted as a function of the relative pressure p/p_0 in the range from $1 \cdot 10^{-6}$ to 0.030 (valid for argon).

$$V_m = 1/a_{Langmuir} \qquad (2)$$

The molecular cross sectional area used for argon is $\sigma_{Ar} = 0.142\ nm^2$.

The micropore volume and the median micropore width were calculated using the model of Saito and Foley as described in the standard DIN 66135-4 [1]. For the calculation, the following values for the model parameters given in Table 1 were used:

Table 1 - Values for the Saito-Foley model parameters [16]

Parameter	Adsorbent (oxide ion)	Adsorptive (argon)	Unit
Temperature T	–	87.3	K
Diameter d	0.276	0.336	nm
Polarisability α	2.5?10-24	1.63 10-24	cm^3
Magnetic susceptibility χ	1.3?10-29	3.25 10-29	cm^3
Density per unit area N	1.31?1015	8.52 1014	(molecules/cm^2)

3.3.2 Micropore measurements: Adsorption of argon at 87 K

The isotherms and the micropore volume distributions of single measurements on BCR-704 and BCR-705 are shown in Figs. 4 to 7 and in Table 2. The porosity data evaluated from these individual measurements are summarised in Table 2. Note that the data in Table 2 are not the certified values. Dry argon (not less than 99.99 % purity) was used as adsorptive and for the cooling bath (liquid argon not less than 99 % purity).

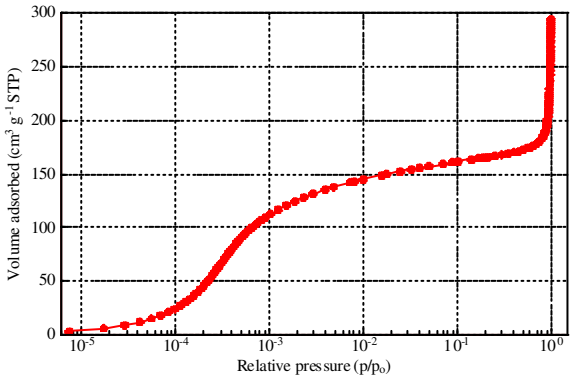

Figure 4 - Adsorption isotherm of argon on BCR-704 at 87 K (Type I isotherm)

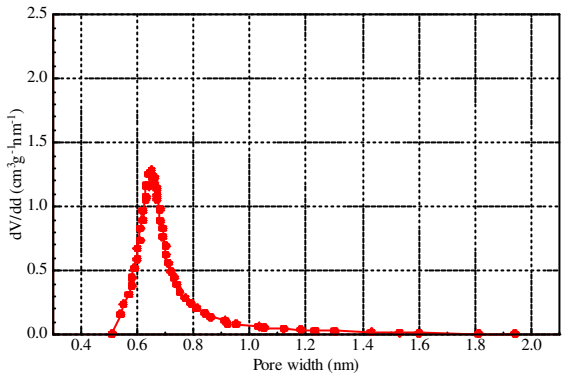

Figure 5 - Pore volume distribution of BCR-704 evaluated from the adsorption isotherm in Fig. 4 using the Saito-Foley model with the model parameter values shown in Table 1

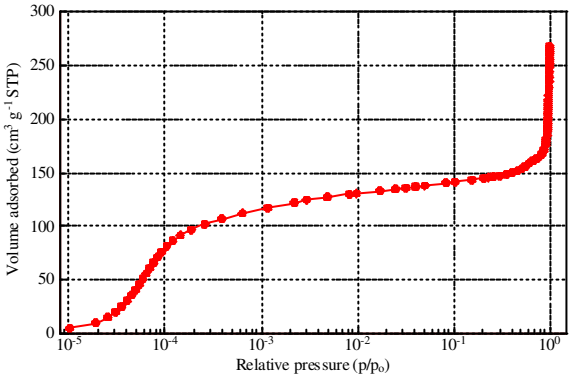

Figure 6 - Adsorption isotherm of argon on BCR-705 at 87 K (Type I isotherm)

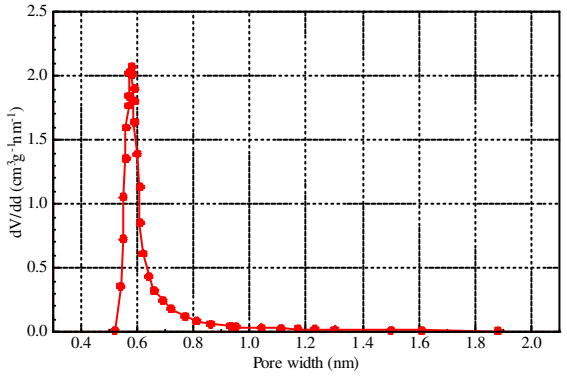

Figure 7 - Pore volume distribution of BCR-705 evaluated from the adsorption isotherm in Fig. 6 using the Saito-Foley model with the model parameter values shown in Table 1

Table 2 - Evaluated porosity properties obtained from the isotherms in Fig. 4 and 6 (results of individual experiments, not the certified values)

Quantity	BCR-704	BCR-705
Micropore volume at p/p_0 = 0.1880 (corresponding to 2 nm pore width)	0.2115 $cm^3\ g^{-1}$	0.1850 $cm^3\ g^{-1}$
Median micropore width	0.66 nm	0.59 nm
Langmuir surface area (all data points up to p/p_0 = 0.030)	586.9 $m^2\ g^{-1}$	514.1 $m^2\ g^{-1}$

4. OUTGASING PROCEDURE

Before measuring physisorption isotherms it is very important to remove adsorbed gases and humidity from the surface area of the materials, in order to receive a clean and "free" surface area without adsorbed layers. On the basis of the thermogravimetric investigations (see Fig. 3), the following outgasing procedure for the selected candidate materials has been applied.

Starting at room temperature, the zeolites are to be heated up to about 350 K (≈ 80 °C) under vacuum. When a residual pressure of 10^{-2} Pa or lower has been achieved at 350 K (≈ 80 °C), carefully increase the temperature up to 390 K (≈ 120 °C) at about one Kelvin per minute. In this temperature interval the main portion of water is expelled. When a residual pressure of 10^{-2} Pa or lower has been achieved, heat in vacuum up to 620 K (≈ 350 °C) in steps of 50 K per 30 minutes. After a residual pressure of 10^{-2} Pa or lower has been reached at 620 K (≈ 350 °C), continue evacuating at 620 K (≈ 350 °C) for between 5 and 16 hours (overnight).

Because it is not desirable to contaminate the analysis manifold with water vapour, it is preferable to outgas in a separate manifold. However, if outgasing has been carried out separately, a re-outgasing of the sample on the analysis port may be required (620 K) after the sample has been transferred from the degas port (see Fig. 8).

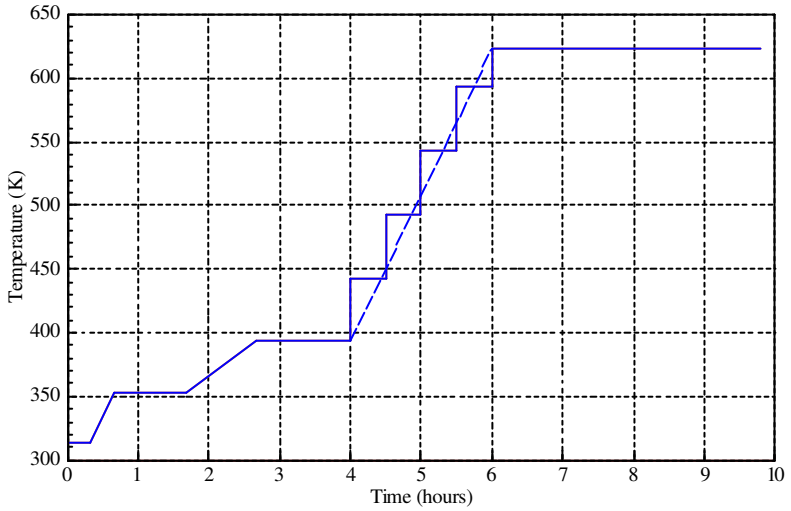

Figure 8 - Heating curve for the pretreatment of BCR-704 and BCR-705 samples

5. HOMOGENISATION AND HOMOGENEITY TESTING

Reference materials (RMs) of any type must be sufficiently uniform (homogeneous) regarding the certified properties when subsampled. In other words, the between-sample variation in properties of the samples should be as low as possible. The minimisation of the between-sample variation can be carried out by subsequent riffling using a rotating sample divider (8 ports) applying the cross-riffling scheme (see below) according to Van der Veen [18]. The first step of this procedure was a riffling step into 8 subsamples. After this step, each of these subsamples was riffled again, yielding 64 small subsamples. Via a recombination of the 64 samples (see Fig. 9), 8 new big samples were formed. Then, 8 additional rifflings were carried out, again yielding 64 small subsamples. For these samples, it may be expected that most of the errors in the first riffling (samples 1 trough 8) have been cancelled out. As was shown by Van der Veen [18], the advantage of this riffling procedure consists in the fact that even if the first 8 samples are not very representative for the batch, the samples A to H will be.

1	2	3	4	5	6	7	8		
⇓	⇓	⇓	⇓	⇓	⇓	⇓	⇓		
1-8	2-7	3-6	4-5	5-4	6-3	7-2	8-1	⇒	H
1-7	2-6	3-5	4-4	5-3	6-2	7-1	8-8	⇒	G
1-6	2-5	3-4	4-3	5-2	6-1	7-8	8-7	⇒	F
1-5	2-4	3-3	4-2	5-1	6-8	7-7	8-6	⇒	E
1-4	2-3	3-2	4-1	5-8	6-7	7-6	8-5	⇒	D
1-3	2-2	3-1	4-8	5-7	6-6	7-5	8-4	⇒	C
1-2	2-1	3-8	4-7	5-6	6-5	7-4	8-3	⇒	B
1-1	2-8	3-7	4-6	5-5	6-4	7-3	8-2	⇒	A

Figure 9 - Recombination table of the cross-riffling scheme

To investigate the resulting homogeneity of the material, it is necessary to separate measurement uncertainty from heterogeneity of the samples. If multiple measurements on the same specimen are possible (in the case of non-destructive investigation methods), this may be achieved by averaging the results. Averaging allows to minimise the effect of measurement uncertainty. Hence, the homogeneity test according to ASTM E 826 - 85 [19] (as recommended in the BCR Guide) requires that a specimen may be measured multiple times.

Unfortunately, multiple measurements in the field of physisorption on porous solids are problematic, since changes of the sample due to the repeated thermal pre-treatment cannot be excluded. Another problem is the long duration of the measurements. For instance, one measurement of the entire adsorption isotherm of the microporous materials selected for certification takes more than 60 hours.

Therefore, information on the homogeneity of the materials BCR-704 and BCR-705 were obtained by comparing the variances of a distinct property for the material under testing with those of a material known to be homogeneous. This method is valid, if the repeatability of the measurement process is nearly the same for both materials. Under this assumption, differences are due to heterogeneity. To decide, whether the variances are significantly different or not, a statistical standard procedure was applied (F-test [20, 21], see in the Annex on pages A4 and A5). As a reference substance the material CRM BAM-PM-103 was used, which is assumed to be homogeneous. This statistical comparison was made for the Langmuir specific surface area. In addition, the standard deviation of the means of independent

determinations of a distinct property carried out with the same instrument was compared with the standard deviation for the same property resulting from the interlaboratory testing. The values of the standard deviation of various measuring series for the Langmuir specific surface area, the micropore volume, and the median micropore width are shown in Tables 3-5.

The comparison between the variation coefficients of the Langmuir surface area of the both materials and that of the reference substance by the F-test method (see pages A4 and A5 in the Annex) indicates that BCR-704 is at least as homogeneous as the reference substance, whereas BCR-705 is less homogeneous than the reference substance. But it can be concluded from Tables 3-5 that the standard deviation due to heterogeneity is small compared to s of the interlaboratory testing. This is true for all three of the porosity properties under test. Hence, both candidate materials can be regarded as sufficiently homogeneous for the certification. In order to comply with the latest requirements in the field of Certification of Reference Materials, the data in Annex I were used to derive an uncertainty contribution accounting for homogeneity related variations. For further details refer to Chapter 7.

Table 3 - Standard deviation of test measurements of the Micropore volume in relation to s (standard deviation of means) from the interlaboratory testing

Substance	Data record	s of data record ($cm^3\ g^{-1}$)	s from interlaboratory testing ($cm^3\ g^{-1}$)
BCR-704	BCR-704-1	0.001066	
	BCR-704-2	0.000922	0.0088
	BCR-704-3	0.00247	
BCR-705	BCR-705-1	0.001057	
	BCR-705-2	0.002179	0.0065
	BCR-705-3	0.001760	

Table 4 - Standard deviation of test measurements of the Median micropore width in relation to s (standard deviation of means) from the interlaboratory testing

Substance	Data record	s of data record (nm)	s from interlaboratory testing (nm)
BCR-704	BCR-704-1	0.001216	
	BCR-704-2	0.000453	0.0087
	BCR-704-3	0.000610	
BCR-705	BCR-705-1	0.019526	
	BCR-705-2	0.001457	0.0113
	BCR-705-3	0.000346	

Table 5 - Standard deviation of test measurements of the Langmuir surface area in relation to s (standard deviation of means) from the interlaboratory testing

Substance	Data record	s of data record ($m^2 g^{-1}$)	s from interlaboratory testing ($m^2 g^{-1}$)
BCR-704	BCR-704-1	3.21	
	BCR-704-2	2.88	25.80
	BCR-704-3	5.50	
BCR-705	BCR-705-1	2.92	
	BCR-705-2	4.89	18.97
	BCR-705-3	3.77	

6. STABILITY TESTING

For monitoring the stability of the materials regarding their porosity properties, the results of the test measurements were plotted in graphs with the time as abscissa (see Figs. 10-12). For comparison, in these graphs the certified values and the standard deviations from the interlaboratory testing are also presented. As it can be seen from the diagrams, all means of the test measurements (except that for the median pore width of the 1997 test series[1]) are lying within the ± s boundaries (standard deviation of means) from the interlaboratory testing. Furthermore, there is no clear drift. Therefore, the materials BCR-704 and BCR-705 can be regarded as sufficiently stable. In order to comply with the latest requirements in the field of Certification of Reference Materials, the data in Annex I were used to derive an uncertainty contribution accounting for stability-related variations. For further details refer to Chapter 7.

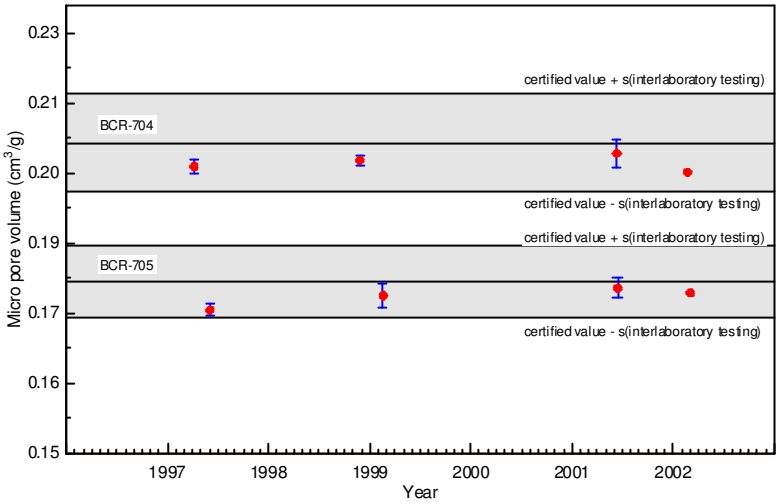

Figure 10 - Long- term stability of the micropore volume of the materials BCR-704 and BCR-705

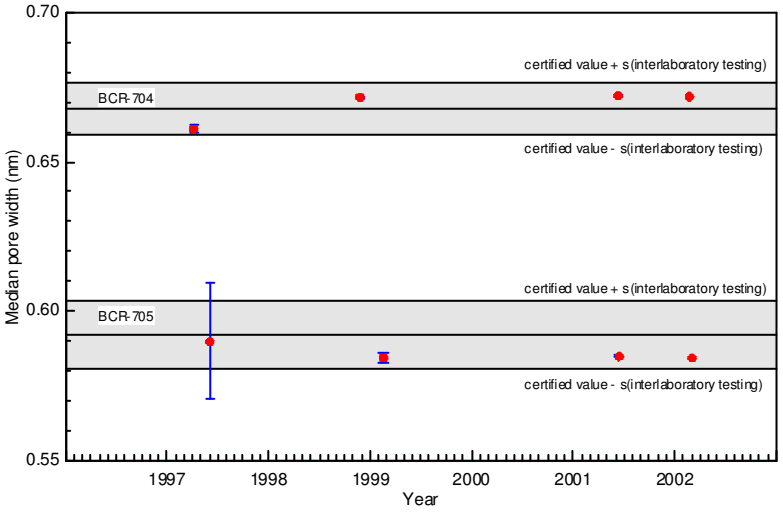

Figure 11 - Long-term stability of the median micropore widths of the materials BCR-704 and BCR-705. Note that due to the insufficient measuring range of the isotherms (only up to p/p0 = 0.015 instead of 0.030) the value of the BCR-705 standard deviation for the 1997 measurements is not comparable with the other standard deviations in this graph.

---

1 The BCR-705 standard deviation for the 1997 measurements is too big due to the insufficient measuring range of the isotherms (only up to p/p0 = 0.015 instead of 0.030). Therefore, it is not comparable with the other standard deviations in Fig. 11.

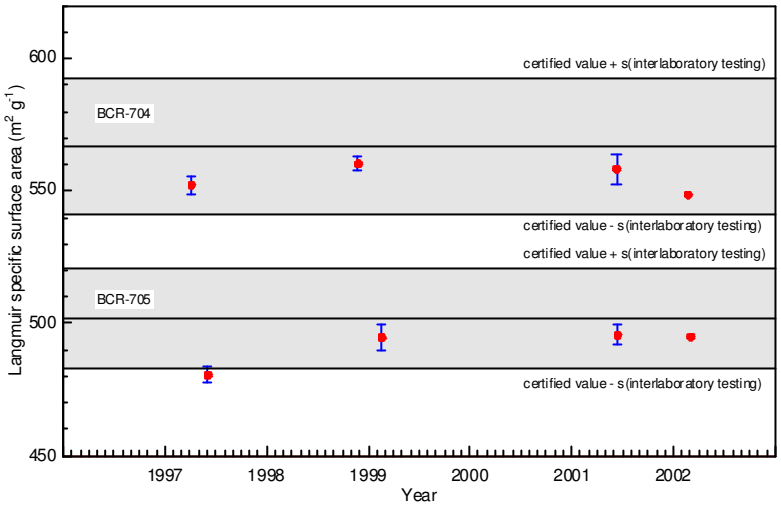

Figure 12 - Long-term stability of the Langmuir surface area of the materials BCR-704 and BCR-705

7. CERTIFICATION PROCEDURE

The certification was carried out according to the BCR guidelines [22] and the relevant ISO guides [23 - 28].

7.1 Selection of the participating laboratories

For testing the measurement capability of the participating laboratories in the field of micropore analysis a proficiency test [29] was arranged. For micropores, no certified reference materials were available. Therefore, an internal test substance (Zeolite 13X) provided by Micromeritics was used as microporous test substance B. As a reference value for substance B, the Langmuir specific surface area was determined from physisorption isotherms (argon/liquid argon at 87 K) by measurements at BAM and Micromeritics using 6 different instruments. The data sets are given in Table A-7 in the Annex.

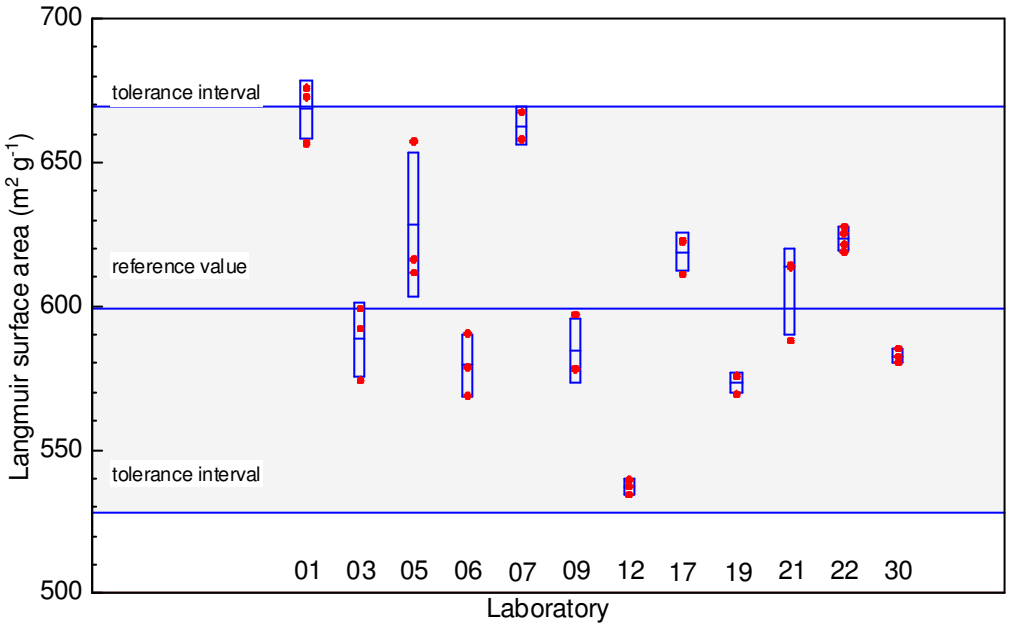

Figure 13 - Results of the proficiency test

Each of the 12 laboratories passed the proficiency test for microporous materials. All of the laboratory means of the Langmuir specific surface area were within the tolerance interval (see Fig. 13). The Langmuir surface area values were calculated from the isotherm data points measured by the participants using a software package developed by the co-ordinator.

7.2 Results of the interlaboratory testing

The values of the porosity properties micropore volume, median micropore width, and Langmuir surface area were calculated by means of a software package of the co-ordinator. The data records for the statistical analysis are given in the Tables A-9 to A-14 in the Annex.

7.2.1 Statistical analysis

Because of using different instruments by the laboratories, very heterogeneous standard deviations were observed. Hence, the "no pooling" option of the BCR recommendations was applied.

The procedure was:

- No outlier test for the standard deviations and no ANOVA, since, as mentioned above, various instruments were used, and heteroscedastic data were assumed a priori.
- The laboratories with only one result value per property to be certified were eliminated because a laboratory mean value was needed.
- Determination of the standard deviation, and a 95 % content tolerance interval at 95 % certainty for the laboratory means.
- Calculation of the certified value (average of laboratory averages).
- Determination of the uncertainty of the certified value (expanded uncertainty according to the GUM including contributions from batch characterisation, homogeneity and stability; coverage factor k=2).

The results of the statistical data analysis are represented in Figs. 14 to 19. The standard graphics output created using the BCR programme SoftCRM 1.0.2 displays the laboratory means with error bars specifying the 95 % confidence interval for each laboratory. Additionally, the certified value $\bar{\bar{x}}$, its 95 % confidence interval (95 % C.I.) and its 95 % tolerance interval (95 % T.I.) are drawn. The numbers in the graphs are in SoftCRM 1.0.2 notation. For the key to the laboratory numbers see the first column in each of the corresponding Tables A-9 to A-14 in the Annex.

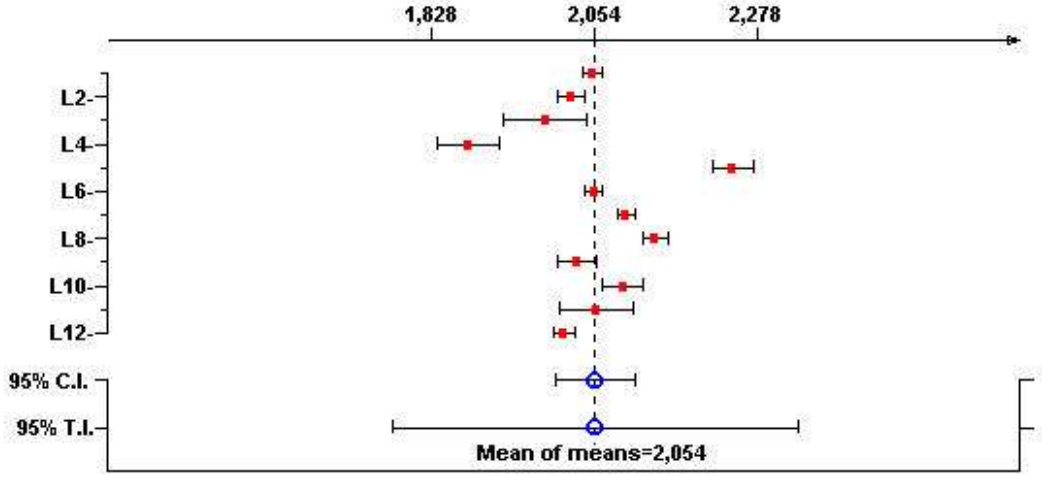

Figure 14 - BCR-704 / Statistical results for the micropore volume [$cm^3\ g^{-1}$]

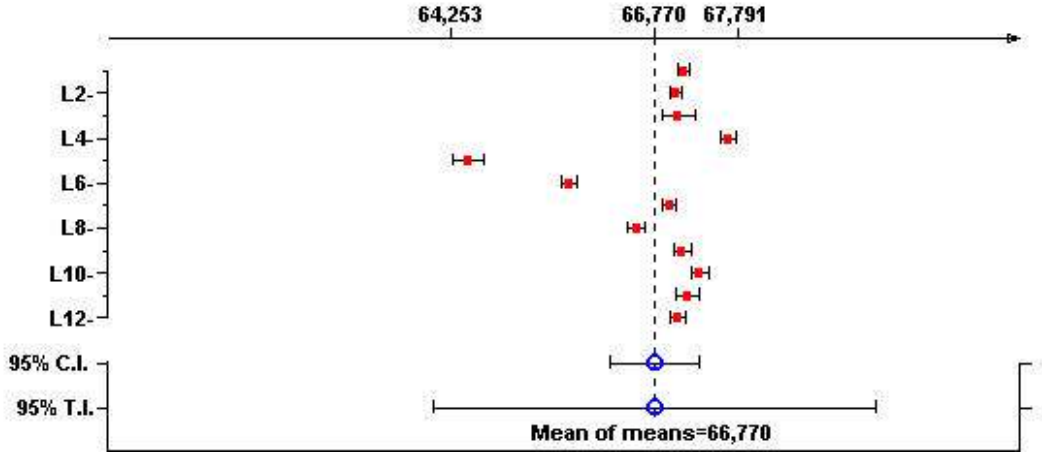

Figure 15 - BCR-704 / Statistical results for the median pore width [nm]

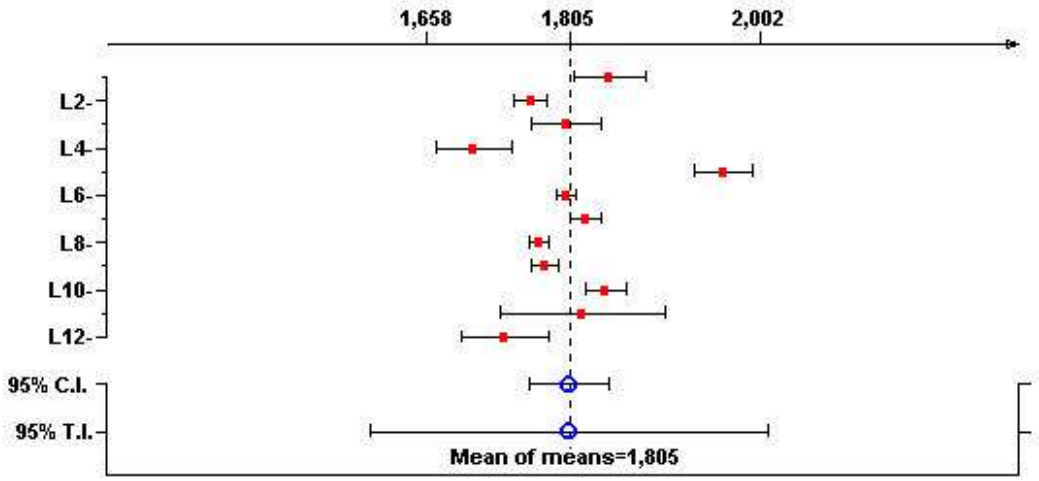

Figure 16 - BCR-704 / Statistical results for the Langmuir surface area [m^2 g^{-1}]

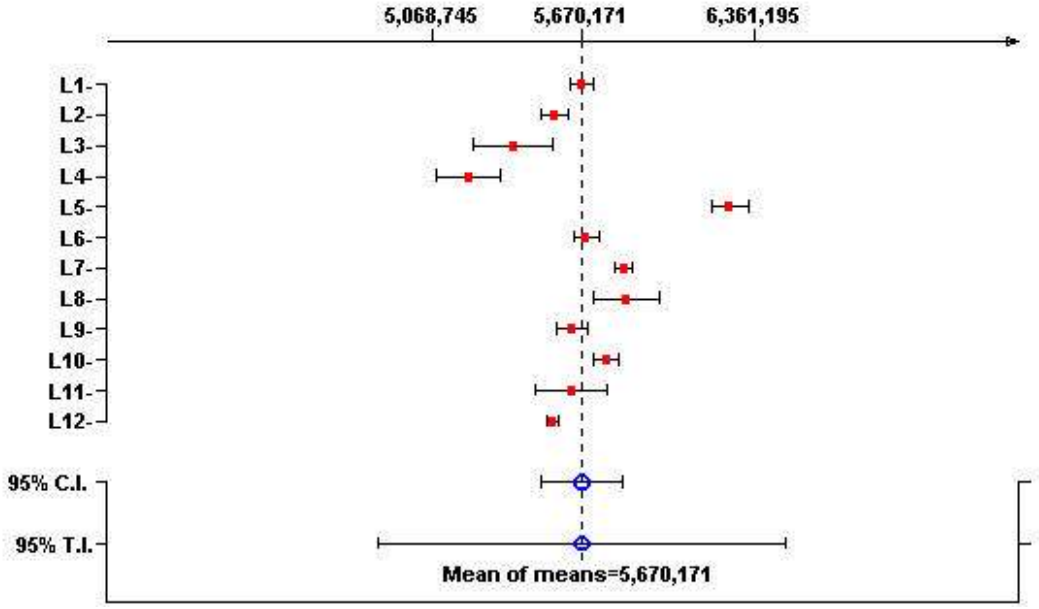

Figure 17 - BCR-705 / Statistical results for the micropore volume [cm^3 g^{-1}]

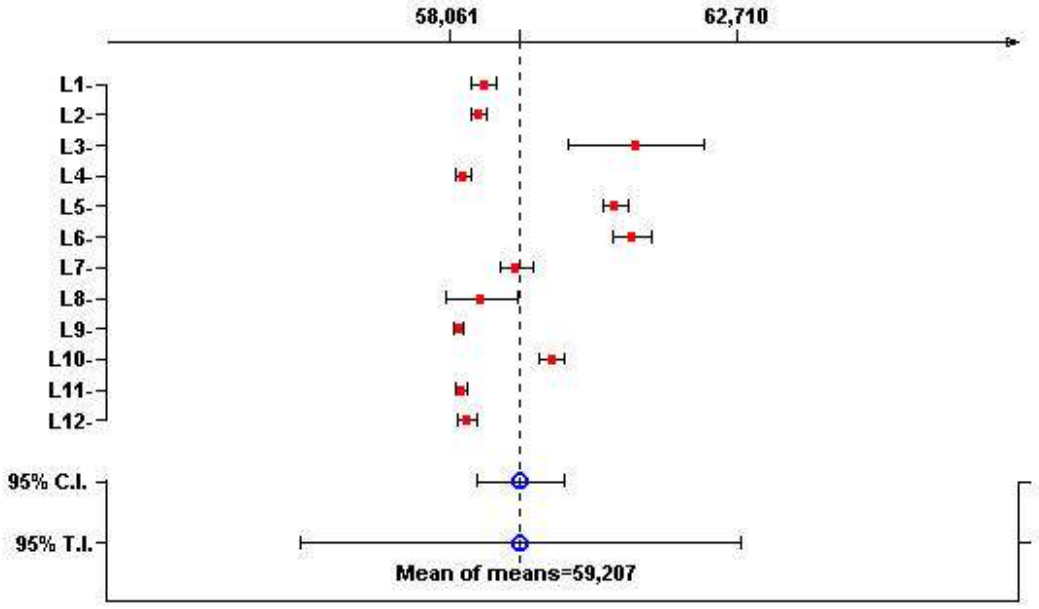

Figure 18 - BCR-705 / Statistical results for the median pore width [nm]

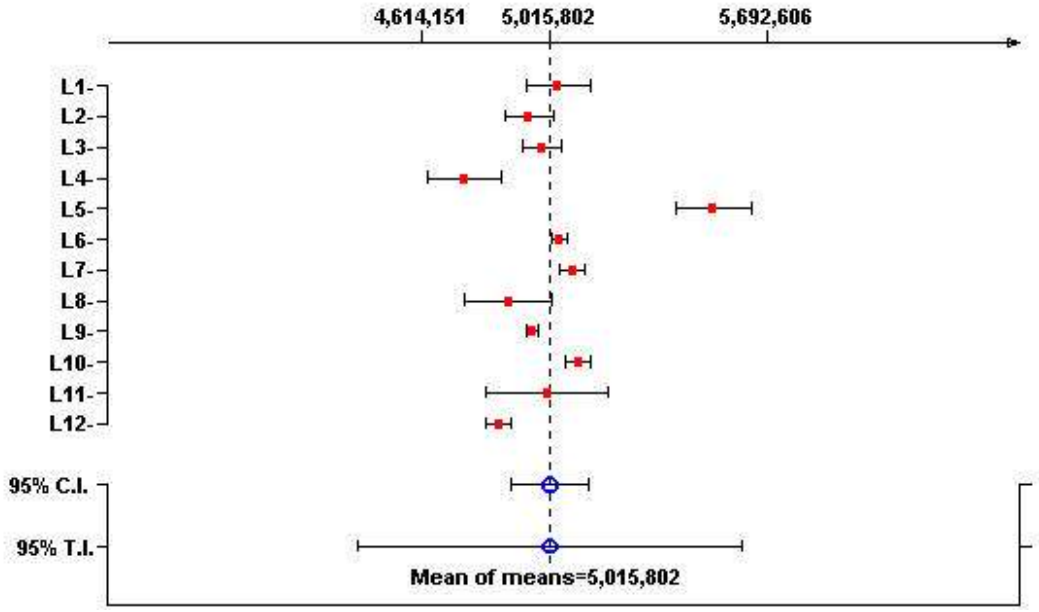

Figure 19 - BCR-705 / Statistical results for the Langmuir surface area [$m^2\ g^{-1}$]

7.3 Certified values and uncertainties

The uncertainty evaluation described hereafter is based on a concept described by Pauwels *et al.* [30 and literature cited] and uses available data discussed in the previous chapters.

7.3.1 Uncertainty evaluation

Based on the data obtained in the stability and homogeneity studies as well as the results in the batch characterisation estimates for u_{bb} (homogeneity), u_{lts} (long-term-stability) and u_{char} (batch characterisation) were obtained and combined according the following equation:

$$U_{CRM} = 2 \cdot \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

Due to the transport conditions selected for dispatch, the uncertainty constituent for short-term stabililty (u_{sts}) is negligible and consequently not included in the overall uncertainty. The estimation of the other uncertainty sources is described below.

7.3.2 Uncertainty source "homogeneity"

The homogeneity study is described in chapter 5. From these data (Annex I), an estimation of u_{bb} was derived from the homogeneity study as described by Linsinger *et al.* [31]. An one-way ANOVA was performed on the data of Annex I. According to this approach, s_{bb} (being the standard deviation between units) or u^*_{bb} (being the upper limit of inhomogeneity that can be hidden by the method repeatability) are used as estimates of u_{bb}. Values for s_{bb} and u^*_{bb} were calculated accordingly:

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}}$$

and

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MSwithin}}},$$

where n is the number of replicates per unit, MS_{within} and $MS_{between}$ the respective mean-of-squares from the ANOVA and $\nu_{MSwithin}$ the degrees of freedom of MS_{within}. If the value of s_{bb} is below the minimum value as determined by the repeatability of the method and the number of replicates performed, u^*_{bb} is used to estimate u_{bb}.

7.3.3 Uncertainty source "stability"

Similarly, a quantitative estimate of the uncertainty related to stability, u_{lts}, was obtained plotting the shelf-life as described elsewhere [31]. The uncertainty was estimated for a shelf-life of 60 months. Appropriate isochronous stability studies have been started while this report is being printed. These studies will allow a confirmation of the forecasted shelf-life.

The estimated uncertainty contribution, u_{lts}, which is included in the combined and expanded uncertainties of the certified values, will be used to establish an expiry date of the certificate. Please refer to the certificate for further details.

7.3.4 Uncertainty source "batch characterisation"

An estimate for u_{char} was derived from the standard error obtained on the mean of laboratories means.

7.3.5 Uncertainty budget

Based on these uncertainty contributions the following uncertainty budget is established:

Table 6 – Uncertainty budgets for BCR-704 and BCR-705. As a rule higher values of s_{bb} and u^*_{bb} were included in the uncertainty budget

	BCR-704		*BCR-705*	
Property value	*Micropore Volume cm^3/g*	*Median micropore width nm*	*Micropore Volume cm^3/g*	*Median micropore width nm*
Mean value	0.2054	0.6677	0.1805	0.5921
u_{char} (%)	1.34	0.92	1.04	0.55
s_{bb} (%)	6.36	0.93	6.13	Not calculable
u^*_{bb} (%)	0.11	0.02	0.24	0.52
u_{lts} (%), 60 months	0.45	0.46	0.90	1.49
U_{CRM} (%)	2.95	2.77	3.37	3.34
U_{CRM}	0.006058	0.018518	0.006076	0.019791

7.3.6 Certified values

The certified values and their associated uncertainties are given in the tables below. Expanded uncertainties (coverage factor k=2) were expressed according to the Guide for the Expression of Uncertainties in Measurement (GUM) [2].

Table 7 – Certified values and Uncertainties. Rounding was done according to the requirements of ISO-Standard 31-0 [32].

Table 8 - BCR-704 (adsorption of argon at 87 K)

Certified property	Certified value	Expanded uncertainty (k=2)	Unit	No. of data sets
Micropore volume	0.205	0.006	$cm^3\ g^{-1}$	12
Median micropore width	0.668	0.019	nm	12

Table 9 - BCR-705 (adsorption of argon at 87 K)

Certified property	Certified value	Expanded uncertainty (k=2)	Unit	No. of data sets
Micropore volume	0.181	0.006	$cm^3\ g^{-1}$	12
Median micropore width	0.592	0.020	nm	12

7.3.7 Indicative values

Besides the data in Tables 8 and 9, Langmuir surface areas were determined. However, data were not found to be suitable for certification and are given as indicative values for the interested reader (Table 10).

Table 10 – Indicative values for Langmuir surface area

Material	Value (mean of means)	Unit	No. of data sets
BCR-704	567	$m^2\ g^{-1}$	12
BCR-705	502	$m^2\ g^{-1}$	12

8. INSTRUCTIONS FOR USE

The sample mass to be analysed should be about 0.2 g, depending on the instrument used (see instructions of instrument producer). Before using BCR-704 and BCR-705, an outgasing procedure is necessary:

Starting at room temperature, the zeolites are to be heated up to about 350 K (≈ 80 °C) under vacuum. When a residual pressure of 10^{-2} Pa or lower has been achieved at 350 K (≈ 80 °C), carefully increase the temperature up to 390 K (≈ 120 °C) with a rate of about one Kelvin per minute. In this temperature range the main portion of water is expelled. When a residual pressure of 10^{-2} Pa or lower has been achieved, heat in vacuum up to 620 K (≈ 350 °C) in steps of 50 K per half an hour. After a residual pressure of 10^{-2} Pa or lower has been reached at 620 K (≈ 350 °C), continue evacuating at 620 K (≈ 350 °C) for at least 5 hours.

Before starting the adsorption measurement, the samples have to be sufficiently degased. To avoid contamining the analysis manifold with water vapour, it is preferable to outgas on a separate manifold. However, if outgassing has been carried out separately, a re-outgasing of the sample on the analysis port may be required (620 K) after the sample has been transferred across.

Attention: Do not use helium to determine the system volume (dead space / free space) until the adsorption measurement is complete.

The material should be stored at normal temperature (20 - 25 °C).

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10. ANNEX I - DATA RECORDS FOR HOMOGENEITY AND STABILITY

10.1 BCR-704

Table A-1: Data record BCR-704-1 (03.03. - 04.04.1997 / ASAP #815)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.198460	0.6602	544.4784
	0.200966	0.6602	551.2242
	0.201329	0.6613	553.0095
	0.202200	0.6615	554.9343
	0.202419	0.6592	555.1323
	0.201813	0.6620	554.1927
	0.201351	0.6626	553.3805
	0.202033	0.6618	554.5314
	0.199974	0.6618	549.9953
	0.201199	0.6591	551.9393
n	10	10	10
$\bar{x}$	0.201174	0.660970	552.281790
s	0.01186	0.001216	3.213980
s^2	0.000001	0.000001	10.329666

Table A-2: Data record BCR-704-2 (07.10. - 25.11.1998 / ASAP #853)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.202688	0.6709	557.9644
	0.201345	0.6715	556.6678
	0.202072	0.6718	559.2774
	0.202254	0.6722	561.2093
	0.202565	0.6716	561.7474
	0.201412	0.6717	558.7094
	0.201630	0.6725	558.8228
	0.202974	0.6721	562.8657
	0.202656	0.6716	561.5552
	0.203963	0.6715	565.6711
	0.201864	0.6718	559.4338
	0.204242	0.6714	566.2114
	0.201536	0.6716	558.3233
	0.201356	0.6723	557.1036
	0.201182	0.6717	557.5765
	0.202855	0.6708	562.0741

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
n	16	16	16
$\bar{x}$	0.202287	0.671688	560.325825
s	0.000922	0.000453	2.883379
s^2	0.000001	0.000000	8.313872

Table A-3: Data record BCR-704-3 (09.05.- 11.06.2001 / ASAP #853)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.202585	0.6724	555.8048
	0.205766	0.6723	561.4463
	0.204493	0.6729	558.9895
	0.205000	0.6715	564.8360
	0.199601	0.6715	550.4357
n	5	5	5
$\bar{x}$	0.203489	0.672120	558.302460
s	0.002470	0.000610	5.503797
s^2	0.000006	0.000000	30.291779

10.2 BCR-705

Table A-4: Data record BCR-705-1 (10.3. - 01.06.1997 / ASAP #853, Isotherm only up to p/p_0=0.015)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.175980	0.5787	481.3136
	0.175825	0.5798	481.5000
	0.176144	0.6208	481.8913
	0.176239	0.6218	481.9779
	0.176401	0.5810	483.1205
	0.172958	0.5808	473.9459
	0.174825	0.5795	478.7643
	0.176029	0.5758	481.5535
n	8	8	8
$\bar{x}$	0.175550	0.589775	480.508375
s	0.001152	0.019526	2.921033
s^2	0.000001	0.000381	8.532436

Table A-5: Data record BCR-705-2 (30.11.1998 - 17.02.1999 / ASAP #853)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.175787	0.5859	489.9702
	0.177481	0.5824	493.4049
	0.181535	0.5842	503.9100
	0.177592	0.5850	492.3848
	0.180819	0.5831	499.7814
	0.175411	0.5828	489.5507
	0.177526	0.5864	494.2493
	0.1788	0.5846	493.7285
n	8	8	8
$\bar{x}$	0.178119	0.584300	494.622475
s	0.002179	0.001457	4.894127
s^2	0.000005	0.000002	23.952474

Table A-6: Data record BCR-705-3 (21.05.-13.06.2001 / ASAP #853)

	Micropore volume ($cm^3\ g^{-1}$)	Median micropore width (nm)	Langmuir surface area ($m^2\ g^{-1}$)
	0.181344	0.5849	499.5290
	0.177891	0.5849	492.0439
	0.179027	0.5843	495.0466
n	3	3	3
$\bar{x}$	0.179421	0.584700	495.539833
s	0.001760	0.000346	3.766847
s^2	0.000003	0.000000	14.189140

10.3 F-Test for the homogeneity testing

10.3.1 Reference substance

Material CRM BAM-PM-103 (alumina type 60)

sample size: $n_{Ref} = 9$

average: $\bar{x}_{Ref} = 158.55$

std: $s_{Ref} = 0.70222$

$cv_{Ref} = s_{Ref} / \bar{x}_{Ref} = 0.004443$

10.3.2 Calculation for BCR-704

Data record BCR-704-1 (03.03. - 04.04.1997 / ASAP #815)

Hypothesis H_0: $\sigma_1 / \mu_1 = \sigma_{Ref} / \mu_{Ref}$

Alternative: $\sigma_1 / \mu_1 > \sigma_{Ref} / \mu_{Ref}$

Langmuir surface area ($m^2\ g^{-1}$)

sample size: n_1 = 10

average: $\bar{x}_1$ = 552.281790

std: s_1 = 3.213980

$cv_1 = s_1/\bar{x}_1$ = 0.005819

$F = cv_1^2/cv_{Ref}^2 = 1.73 < 2.56 = F_{9,8;0.90}$

Hypothesis H_0 cannot be rejected with 90 % certainty.

(The coefficients of variation are not significantly different.)

Data record BCR-704-2 (07.10. - 25.11.1998 / ASAP #853)

Hypothesis H_0: $\sigma_2 / \mu_2 = \sigma_{Ref} / \mu_{Ref}$

Alternative: $\sigma_2 / \mu_2 > \sigma_{Ref} / \mu_{Ref}$

Langmuir surface area ($m^2\ g^{-1}$)

sample size: n_2 = 16

average: $\bar{x}_2$ = 560.325825

std: s_2 = 2.883379

$cv_2 = s_2/\bar{x}_2$ = 0.005146

$F = cv_2^2/cv_{Ref}^2 = 1.35 < 2.46 = F_{15,8;0.90}$

Hypothesis H_0 cannot be rejected with 90 % certainty.

(The coefficients of variation are not significantly different.)

10.3.3 Calculation for BCR-705

Data record BCR-705-1 (10.3. - 01.06.1997 / ASAP #853)

Hypothesis H_0: $\sigma_1 / \mu_1 = \sigma_{Ref} / \mu_{Ref}$

Alternative: $\sigma_1 / \mu_1 > \sigma_{Ref} / \mu_{Ref}$

Langmuir surface area ($m^2\ g^{-1}$)

sample size: n_1 = 8

average: $\bar{x}_1$ = 480.508375

std: s_1 = 2.921033

$cv_1 = s_1/\bar{x}_1$ = 0.006079

$F = cv_1^2/cv_{Ref}^2 = 1.88 < 3.50 = F_{7,8;0.95}$

Hypothesis H_0 cannot be rejected with 90 % certainty.

(The coefficients of variation are not significantly different.)

Data record BCR-705-2 (30.11.1998 - 17.02.1999 / ASAP #853)

Hypothesis H_0: $\sigma_2 / \mu_2 = \sigma_{Ref} / \mu_{Ref}$

Alternative: $\sigma_2 / \mu_2 > \sigma_{Ref} / \mu_{Ref}$

Langmuir surface area ($m^2\ g^{-1}$)

sample size:	n_2	=	8
average:	$\bar{x}_2$	=	494.622475
std:	s_2	=	4.894127
	$cv_2 = s_2/\bar{x}_2$	=	0.009895

$F = cv_2^2/cv_{Ref}^2 = 4.99 > 3.50 = F_{7,8;0.95}$

$< 6.18 = F_{7,8;0.99}$

Hypothesis H_0 is rejected with 95 % certainty, but cannot be rejected with 99 % certainty.

(The coefficients of variation are significantly different at the 5 % level.)

11. ANNEX II - DATA RECORDS FOR THE PROFICIENCY TESTING

Table A-7: Measurements for the determination of the reference value Substance B (zeolite 13X)

No.	Instrument	Langmuir specific surface area ($m^2 g^{-1}$)	Mean ($m^2 g^{-1}$)	Standard deviation ($m^2 g^{-1}$)
A	ASAP 2010 # 340	602.341	–	–
	(BAM)			
B	ASAP 2010 # 815	593.497	579.8	8.865
	(BAM)	579.162		
		585.351		
		574.759		
		587.389		
		572.340		
		580.162		
		565.926		
C	ASAP 2010 # 853	582.402	582.7	2.505
	(BAM)	585.313		
		580.326		
D	Autosorb-1	625.395	623.3	3.901
	(BAM)	627.585		
		621.507		
		618.863		
E	Sorptomatic 1990	614.223	605.3	14.982
	(BAM)	613.712		
		588.022		
F	ASAP 2010	595.977	600.1	9.635
	(Micromeritics)	611.140		
		593.261		

Evaluation of the Langmuir specific surface area as a reference value

number of laboratories: $n = 6$ (A to F)

Reference value : $\bar{\bar{x}} = 598.9\ m^2 g^{-1}$

standard deviation $s = 15.978\ m^2 g^{-1}$

uncertainty $s / \sqrt{n} = 6.5\ m^2 g^{-1}$

95 % confidence interval $598.9 \pm 16.8\ m^2 g^{-1}$

95 % tolerance interval $598.9 \pm 70.5\ m^2 g^{-1}$

Table A-8: Results of the proficiency testing (measurements of substance B)

Laboratory No.	Instrument	Langmuir specific surface area ($m^2 g^{-1}$)	Mean ($m^2 g^{-1}$)	Standard deviation ($m^2 g^{-1}$)
01	Autosorb-1MP	675.8048 672.6616 656.5260	668.3308	10.3433
03	ASAP 2010	592.0296 574.0173 598.9797	588.3422	12.8833
05	Autosorb-3MP	657.2050 611.3999 616.1757	628.2602	25.1804
06	ASAP 2010	590.3626 568.5778 578.6253	579.1886	10.9034
07	Omnisorb (TM) 100	657.9908 667.3860	662.6884	6.6434
09	Omnisorb 360	578.0760 577.9310 596.8932	584.3001	10.9062
12	ASAP 2010	539.3736 534.2392 537.1153	536.9094	2.5734
17	Sorptomatic 1990	622.7558 622.3324 610.9269	618.6717	6.7105
19	ASAP 2010	569.2300 575.4859 575.4363	573.3841	3.5976
20	ASAP 2010	585.2054 574.6162 587.2423 572.1978 542.0170 580.0176 579.0182 593.3494	576.7080	15.6049
21	Sorptomatic 1990	613.9671 613.4674 587.7802	605.0716	14.9768
22	Autosorb-1C	625.2391 627.4286 621.3520 618.7086	623.1821	582.5352
30	ASAP 2010	582.2567 585.1672 580.1816	582.5352	2.5044

12. ANNEX III - DATA SETS FOR THE CERTIFICATION

The data assessment assuming heteroscedastic data sets were carried out using he BCR programme SoftCRM 1.0.2 with the option no pooling. The physical properties micropore volume, median pore with and Langmuir surface area were calculated by means of an own software package of the co-ordinator. The Tables A4 to A9 contain the data sets and statistical results for each laboratory participated in the interlaboratory comparison. The data listings are in SoftCRM 1.0.2 standard notation. The key to the laboratory numbers is in the first column of each table. The sequence of data columns is as follows:

No.	serial number for current calculation
Labs	laboratory identifier i
Means	average for laboratory No. i
SD	standard deviation for laboratory No. i
Samples	individual values of laboratory No. i

12.1 Material BCR-704

Table A-9: *BCR-704 / Experimental data sets for the Micropore volume*

No.	Labs	Means [cm^3/g]	SD [cm^3/g]	Samples [cm^3/g]					
L01	- 01	0.2050	0.0012	0.2048	0.2065	0.2062	0.2035	0.2040	0.2051
L02	- 03	0.2020	0.0015	0.2028	0.2032	0.2027	0.2020	0.1994	
L03	- 05	0.1985	0.0055	0.2037	0.2059	0.1964	0.1906	0.1971	0.1972
L04	- 06	0.1879	0.0040	0.1828	0.1851	0.1907	0.1928	0.1853	0.1905
L05	- 07	0.2245	0.0026	0.2237	0.2220	0.2275	0.2278	0.2237	0.2220
L06	- 09	0.2052	0.0012	0.2035	0.2041	0.2063	0.2067	0.2049	0.2056
L07	- 12	0.2096	0.0011	0.2100	0.2106	0.2083	0.2111	0.2091	0.2087
L08	- 17	0.2137	0.0016	0.2135	0.2137	0.2145	0.2160	0.2111	0.2134
L09	- 19	0.2029	0.0025	0.2011	0.1987	0.2048	0.2051	0.2031	0.2043
L10	- 21	0.2092	0.0028	0.2105	0.2095	0.2123	0.2083	0.2042	0.2104
L11	- 22	0.2057	0.0048	0.2078	0.2010	0.2084	0.2098	0.2087	0.1982
L12	- 30	0.2011	0.0014	0.2015	0.1992	0.2004	0.2006	0.2035	0.2013

Table A-10: *BCR-704 / Experimental data sets for the Median micropore width*

No.	Labs	Means [nm]	SD [nm]	Samples [nm]					
L01	- 01	0.6712	0.0006	0.6713	0.6714	0.6716	0.6701	0.6719	0.6712
L02	- 03	0.6703	0.0006	0.6713	0.6699	0.6704	0.6699	0.6700	
L03	- 05	0.6707	0.0019	0.6717	0.6690	0.6734	0.6716	0.6690	0.6692
L04	- 06	0.6767	0.0009	0.6771	0.6779	0.6772	0.6768	0.6759	0.6758
L05	- 07	0.6447	0.0019	0.6429	0.6447	0.6465	0.6472	0.6425	0.6444
L06	- 09	0.6572	0.0009	0.6574	0.6584	0.6570	0.6557	0.6576	0.6567
L07	- 12	0.6695	0.0008	0.6701	0.6709	0.6691	0.6691	0.6689	0.6689
L08	- 17	0.6654	0.0010	0.6658	0.6649	0.6664	0.6665	0.6638	0.6652
L09	- 19	0.6711	0.0010	0.6715	0.6692	0.6718	0.6711	0.6717	0.6714
L10	- 21	0.6733	0.0010	0.6747	0.6738	0.6736	0.6736	0.6719	0.6722
L11	- 22	0.6717	0.0014	0.6724	0.6732	0.6724	0.6707	0.6722	0.6695

L12 - 30	0.6706	0.0009	0.6716	0.6694	0.6703	0.6699	0.6710	0.6713

Table A-11: *BCR-704 / Experimental data sets for the Langmuir surface area*

No. Labs	Means [m^2/g]	SD [m^2/g]	Samples [m^2/g]					
L01 - 01	566.9610	4.4603	566.7947	571.7852	567.7470	561.5201	571.7527	562.1662
L02 - 03	556.1007	4.2914	558.9303	559.5234	557.0974	556.1283	548.8242	
L03 - 05	539.3912	15.1107	547.5752	561.6193	535.8175	515.6783	537.2628	538.3939
L04 - 06	521.4648	12.1637	506.8745	511.5612	529.3095	538.2720	514.8748	527.8969
L05 - 07	626.1846	7.1237	622.8388	615.5709	636.1195	628.2301	630.7130	623.6351
L06 - 09	568.7024	4.7752	562.1454	565.1265	568.1696	575.3529	569.0282	572.3920
L07 - 12	583.6467	3.2321	584.9379	586.9211	580.0364	587.5049	581.6524	580.8277
L08 - 17	584.6059	12.6286	576.5717	574.9267	571.9810	584.7584	596.2225	603.1751
L09 - 19	562.7374	6.0672	562.9534	552.5629	561.4308	569.5374	561.6104	568.3296
L10 - 21	576.6868	4.6737	577.2009	573.6530	583.3919	569.6339	577.4364	578.8049
L11 - 22	562.6595	13.7568	566.5465	546.0013	572.1609	579.0172	566.3659	545.8650
L12 - 30	555.0636	2.3161	557.3680	551.2631	553.5558	555.5255	555.5133	557.1560

12.2 Material BCR-705

Table A-12: *BCR-705 / Experimental data sets for the Micropore volume*

No. Labs	Means [cm^3/g]	SD [cm^3/g]	Samples [cm^3/g]					
L01 - 01	0.1847	0.0036	0.1848	0.1862	0.1866	0.1808	0.1803	0.1895
L02 - 03	0.1765	0.0016	0.1746	0.1759	0.1758	0.1766	0.1769	0.1794
L03 - 05	0.1802	0.0034	0.1794	0.1855	0.1785	0.1805	0.1820	0.1754
L04 - 06	0.1706	0.0037	0.1723	0.1715	0.1692	0.1767	0.1665	0.1676
L05 - 07	0.1964	0.0029	0.1949	0.1942	0.2002	0.1949	0.2002	0.1942
L06 - 09	0.1802	0.0009	0.1816	0.1792	0.1796	0.1801	0.1796	0.1811
L07 - 12	0.1821	0.0015	0.1832	0.1811	0.1846	0.1821	0.1807	0.1810
L08 - 17	0.1773	0.0010	0.1761	0.1786	0.1779	0.1777	0.1762	0.1775
L09 - 19	0.1780	0.0013	0.1778	0.1798	0.1788	0.1768	0.1763	0.1782
L10 - 21	0.1843	0.0021	0.1829	0.1853	0.1870	0.1859	0.1816	0.1831
L11 - 22	0.1819	0.0081	0.1903	0.1880	0.1733	0.1888	0.1725	0.1782
L12 - 30	0.1739	0.0042	0.1658	0.1743	0.1731	0.1775	0.1762	0.1762

Table A-13: *BCR-705 / Experimental data sets for the Median micropore width*

No. Labs	Means [nm]	SD [nm]	Samples [nm]					
L01 - 01	0.5862	0.0018	0.5856	0.5884	0.5837	0.5857	0.5852	0.5883
L02 - 03	0.5853	0.0013	0.5835	0.5859	0.5852	0.5858	0.5845	0.5872
L03 - 05	0.6107	0.0104	0.6148	0.6149	0.5981	0.6271	0.6067	0.6026
L04 - 06	0.5829	0.0011	0.5820	0.5828	0.5825	0.5845	0.5838	0.5816
L05 - 07	0.6074	0.0020	0.6070	0.6056	0.6101	0.6065	0.6097	0.6056
L06 - 09	0.6102	0.0029	0.6128	0.6082	0.6136	0.6108	0.6057	0.6100
L07 - 12	0.5914	0.0025	0.5881	0.5952	0.5916	0.5910	0.5896	0.5928

L08 - 17	0.5857	0.0056	0.5861	0.5840	0.5965	0.5806	0.5834	0.5839
L09 - 19	0.5821	0.0008	0.5814	0.5830	0.5826	0.5811	0.5817	0.5827
L10 - 21	0.5971	0.0019	0.5980	0.5977	0.5946	0.5959	0.5964	0.6001
L11 - 22	0.5824	0.0010	0.5818	0.5826	0.5824	0.5826	0.5812	0.5841
L12 - 30	0.5835	0.0015	0.5812	0.5847	0.5831	0.5836	0.5830	0.5853

Table A-14: *BCR-705 / Experimental data sets for the Langmuir surface area*

No. Labs	Means [m^2/g]	SD [m^2/g]	Samples [m^2/g]					
L01 - 01	504.0854	9.5903	503.3758	513.205	503.7852	493.8572	493.5419	516.7475
L02 - 03	494.8895	7.0835	485.0312	494.7123	495.9523	489.4827	498.9234	505.2348
L03 - 05	498.9687	6.0105	494.4796	507.6936	495.0971	503.2701	501.1067	492.1648
L04 - 06	474.9795	10.9588	481.5847	475.9769	471.2363	492.2972	461.4151	467.3670
L05 - 07	552.5606	11.5074	542.1738	542.3475	569.2606	548.7545	564.3772	548.4501
L06 - 09	504.4148	2.5799	507.1981	501.9391	501.2783	506.9429	503.3142	505.8161
L07 - 12	508.3821	3.4979	510.2714	505.2091	514.1279	509.1870	505.8083	505.6889
L08 - 17	488.4914	13.0664	469.0816	487.1603	499.8479	484.8737	483.8443	506.1404
L09 - 19	496.0322	1.6074	497.0278	497.2334	496.6185	494.3476	493.6526	497.3133
L10 - 21	510.2373	3.9726	507.2126	513.4369	514.8679	512.6458	504.8616	508.3990
L11 - 22	500.5051	18.4597	515.4735	516.7317	482.5743	518.9399	479.5229	489.7884
L12 - 30	485.4156	3.9034	489.9159	482.9335	478.9165	487.5544	486.2588	486.9145

13. ANNEX IV - INSTRUMENTS AND PRODUCERS

Table A-15: Instruments used by the participants in the interlaboratory comparison

Type of Instrument	*Producer*	∑
ASAP 2010	Micromeritics	5
Sorptomatic 1990	Carlo Erba	2
Autosorb-1/MP	Quantachrome	1
Autosorb-3/MP	Quantachrome	1
Autosorb-1/C	Quantachrome	1
Omnisorb 360	Coulter	1
Omnisorb (TM) 100 CX	Coulter	1

European Commission

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Certification of the specific micropore volume and the median micropore width of two microporous reference materials according to Draft-DIN 66135-4, BCR-704, BCR-705
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Abstract

This report describes the certification of the specific micropore volume and the median micropore width of two microporous reference materials (zeolites with 1-2 % clay as binder) according to Draft-DIN 66135-4 [1]. The adsorptive used for both materials was argon at the temperature of liquid argon. The report contains all the results of the 10 participating laboratories using 12 instruments. Furthermore, the data concerning the homogeneity and the stability studies are summarised. The Langmuir specific surface area and the density measured by helium gas pycnometry are given as indicative values.
Certified values were accompanied by an expanded uncertainty according to the requirements laid down in the Guide for the Expression of Uncertainty in Measurement (GUM) [2].

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